Renewable and Sustainable Energy Reviews 16 (2012) 2366–2372

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review on current status of hydrogen production from bio-oil

Shyamsundar Ayalur Chattanathan, Sushil Adhikari*, Nourredine Abdoulmoumine

Department of Biosystems Engineering, Auburn University, Auburn, AL 36849, USA

ARTICLE INFO

Article history:
Received 3 June 2011
Accepted 16 January 2012
Available online 20 March 2012

Keywords:
Bio-oil
Catalyst
Steam to carbon ratio
Steam reforming
Thermodynamic analysis

ABSTRACT

Increase in energy demand and growing environmental awareness has increased interest for alternative renewable energy sources over the last few years. Hydrogen produces only water during combustion, and therefore, it is seen as an alternative fuel for locomotive application. Nonetheless, hydrogen is not an energy source; rather it is an energy carrier. Different techniques are being explored to find an economical way of generating hydrogen from renewable resources. Hydrogen production from water using sunlight is still expensive. Biomass is another alternative to produce hydrogen. Bio-oil derived from biomass using a fast pyrolysis is a potential source for hydrogen production. Although different techniques have been employed to produce hydrogen from bio-oil, significant effort has been put into steam reforming process. This paper reviews major hydrogen production techniques with a great deal of importance given to steam reforming. The important factors that are known to affect hydrogen yield are temperature, steam to carbon ratio, and catalyst type. Literature review of bio-oil steam reforming technique has been done, and a comparison of experimental conditions has been carried out. However, as a major shortcoming, this technique is accompanied by the formation of carbonaceous deposits over the catalyst surface rendering it inactive and requiring frequent regeneration. Coke formation has been cited as the major disadvantage of bio-oil reforming, and it is more pronounced when Ni based catalysts are used.

Contents

1. Introduction

Renewable and alternative fuels have attracted significant interest as a remedy for greenhouse gases emitted from fossil fuels and uprising price of petroleum fossil based fuels. Among many renewable fuels investigated, hydrogen is of utmost importance because

* Corresponding author. Tel.: +1 334 844 3543; fax: +1 334 844 3530.
E-mail address: sushil.adhikari@auburn.edu (S. Adhikari).

1364-0321/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.rser.2012.01.051

of its highest energy content per weight (120 MJ/kg) [1]. Additionally, when produced from biomass, hydrogen does not pose any environmental problems and does not increase atmospheric carbon dioxide (CO_2) emissions [2]. Although several methods of hydrogen production exist, the emphasis of this paper is on hydrogen production from bio-oil produced from biomass fast pyrolysis. Fast pyrolysis is the degradation of biomass at around 500 °C in the absence of oxygen to yield a liquid fuel (hereafter, bio-oil), as well as solid (biochar) and noncondensable gases [3–5]. Bio-oil (also called pyrolysis oil or biocrude) has an energy density of around 20 MJ/m^3, which is about ten times that of biomass, making bio-oil an excellent alternative source of energy [6].

Bio-oil is a dark to brown organic liquid containing degradation products of the three main components, namely cellulose, hemicelluloses and lignin. The composition of bio-oil varies depending on the biomass source as well as the process conditions. Nonetheless, it typically consists of water and a complex mixture of organic compounds such as hydroxyaldehydes, hyroxyketones, sugars, carboxylic acids and phenolics from the breakdown of biomass carbohydrates and lignin [7]. Its main elemental constituents are carbon (C), hydrogen (H), and oxygen (O), and hence its empirical chemical formula is given as $C_nH_mO_k{\cdot}xH_2O$ [8]. Bio-oil can be separated into organic and aqueous phases by adding water to it and volatile compounds constitute about 60% of bio-oils [9].

Bio-oil has numerous applications which includes its usage in boilers for heat and electricity, in engines and turbines for electricity, in chemicals production such as phenols, organic acids, and oxygenates or in transportation fuel production [4]. However, bio-oil derived transportation fuels require expensive upgrading techniques, and this route is currently less attractive for motor fuels production. To alleviate this disadvantage, reforming of bio-oil has been proposed and employed to produce hydrogen, another viable fuel for the future.

This paper reviews the state-of-the-art of hydrogen production from bio-oil with the main focus on steam reforming. Furthermore, the paper discusses the influence of different process parameters such as temperature, steam to carbon ratio, catalysts type, reactor design and others on hydrogen yield. The paper addresses some of the challenges faced by reforming of bio-oil for hydrogen production including possible remedies.

2. Bio-oil feedstock and characterization

Bio-oils have been produced from different biomass feedstocks such as corn stover [10] rice husk [11,12], saw dust [13,14], wood [15] [16], barley straw [17], poultry litter [18] and many others. A detailed review on bio-oil production techniques and its properties can be found elsewhere [19]. Physical and chemical properties of bio-oil are highly influenced by the composition of biomass. For example, Wang et al. [8] reported that sawdust has 54.5% C, 6.7% H and 38.7% O, while rice husk has 41% C, 7.4% H and 51.2% O and cotton stalk has about 42.3% C, 7.9% H and 49.4% O. Hydrogen yield is also affected by the chemical composition of bio-oils and therefore, the feedstock used to generate bio-oil plays a vital role in hydrogen production. Estimating the bio-oil composition is important in calculating the stoichiometric hydrogen (H_2) yield, which is discussed in the next section. Typical properties of bio-oil are summarized in Table 1 [20]. It is interesting to note that bio-oils are acidic in nature and the pH value is also highly dependent on the biomass type. For example, the bio-oils generated from sawdust, rice husk and cotton stalk had pH of about 2.1, 3.2, and 3.3, respectively [8].

Table 1
Typical properties of bio-oil.

Water content	15–30
pH	2.5
Specific gravity	1.2
HHV (MJ/kg)	16–19
Viscosity, at 500 °C (cP)	40–100

Elemental analysis, wt%	
C	54–58
H	5.5–7
N	0–0.2
O	35–40
Ash	0–0.2

3. Hydrogen production from bio-oil

Hydrogen is the most abundant element in the universe and the third most abundant element on the earth's surface [21]. It is very light, highly flammable and burns with pure oxygen producing heat and water in contrast to fossil fuels which produce CO_2 on combustion [21]. It has a very high energy content of 120 MJ kg^{-1}compared to that of gasoline (44.4 MJ kg^{-1}). Hydrogen is considered as an energy carrier instead of an alternative fuel because it is not available freely [21–23]. Bio-oil comprises good percentage of hydrogen and is therefore utilized in hydrogen production. DynaMotive Energy Systems Corporation, Ensyn Group Inc., and BTG Biomass Technology Group are three major bio-oil producers [24]. There are different techniques by which hydrogen is produced from bio-oil but the majority of the studies are focused on steam reforming process. Therefore, in-depth review on bio-oil steam reforming is presented here.

3.1. Steam-reforming

Steam reforming is an efficient process for hydrogen production and has been in practice since 1930 [25]. Standard Oil Co., USA began the first steam reforming plant in 1930 with light alkanes as feed [26]. It is an endothermic process in which the substrate is treated with steam in the presence of catalyst to produce carbon monoxide (CO), CO_2 and hydrogen (H_2) [27]. The chemical reactions for steam reforming of bio-oils are given below [28]:

$$C_nH_mO_k + (n-k)H_2O \rightarrow nCO + (n + m/2 - k)H_2 \quad (1)$$

The CO can be further converted to CO_2 by the water–gas shift reaction (Eq. (2)).

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

Overall reaction is given as presented in Eq. (3).

$$C_nH_mO_k + (2n-k)H_2O \rightarrow nCO_2 + (2n + m/2 - k)H_2 \quad (3)$$

The amount of biological material that contains 1 g atom of carbon is termed as 1 mol of the biological material [29]. Table 2 summarizes a comparison of the moles of H_2 produced per mole of the source in different methods which includes steam reforming, partial oxidation and supercritical water reforming of various substrates like ethanol, ethyl lactate, glycerol, and bio-oil and its aqueous fraction. On an average, it is found that 1 mol of bio-oil substrate produces 2 mol of H_2.

4. Thermodynamic analysis

The composition of an exit gas stream and important process parameters affecting H_2 yield are usually predicted by the thermodynamic analysis. Vagia and Lemonidou [34] performed a detailed thermodynamic analysis of H_2 production via steam reforming with ASPEN 11.1 using acetic acid, ethylene glycol, and acetone as model compounds of bio-oil. Peng–Robinson property method and RGibbs reactor were selected with equilibrium compositions being

Table 2
Theoretical estimation of number of moles of H_2 produced per mole of the source.

Substrate/source	Technique	Moles of H_2 produced/mole of source (theoretical)	Reference
Bio-oil/poplar wood	Steam reforming	2.2	[30]
Bio-oil/pine wood	Steam reforming	1.73	[30]
Bio-oil/hardwood	Steam reforming	2.12	[30]
Aqueous fraction of bio-oil	Steam reforming	1.92	[11]
Bio-oil/sawdust	Steam reforming	2.2	[8]
Bio-oil/rice husk	Steam reforming	2.15	[8]
Bio-oil/cotton stalk	Steam reforming	2.24	[8]
Bio-oil/poplar wood (after cold storage for long time)	Steam reforming	2.19	[31]
Bio-oil/poplar wood	Partial oxidation	1.66	[31]
Ethanol	Steam reforming	3	[1]
Ethyl lactate	Partial oxidation	1	[32]
Glycerol	Steam reforming	2.33	[27]
Glycerol	Super critical water reforming	2.33	[33]

computed by the minimization of Gibb's free energy. The important specifications fed into the software included reactant and product inlet composition, inlet temperature, pressure, reaction temperature, and steam to fuel (S/F) ratio. A study from Vagia and Lemonidou [34] showed that equilibrium concentrations of ethane, ethylene, acetylene and other oxygenated compounds in the product stream were negligible. It was established that H_2 yield was favored at increased temperatures and S/C (steam to carbon ratio) at atmospheric pressure. At optimum conditions of 627 °C, atmospheric pressure and S/C = 3 (steam to carbon ratio), 0.208 kmol/s of the mixture of the model compounds (acetic acid, ethylene glycol and acetone at 4:1:1 molar ratios) yielded about 1 kmol/s of hydrogen. No coke formation was reported at temperatures higher than 327 °C. Vagia and Lemonidou [34] also established that bio-oil can be thermally decomposed to form a mixture of gases containing methane (CH_4), H_2, CO, CO_2 and water (H_2O).

Similar thermodynamic analysis was done by the same research group for H_2 production via autothermal reforming with the same model compounds [35]. They reported a maximum yield at 627 °C but 20% lesser than the yield obtained by the steam reforming. Aktas et al. [36] conducted thermodynamic analysis of steam reforming using isopropyl alcohol, lactic acid and phenol as model compounds of bio-oil at temperatures from 327 °C to 927 °C, S/F ratio from 4 to 9 and total pressure of 30 bar. The fact that H_2 yield increased with increasing temperature and S/F ratio was confirmed.

5. Catalysts

Steam reforming of bio-oils is usually carried out in the presence of a catalyst which not only increases the reaction rate but also helps achieving equilibrium faster. Catalytic reforming of bio-oils has been studied by Chornet group [6,37–41]. Galdámez et al. [2] prepared Ni–Al catalysts by co-precipitation and studied the extent to which loading of La_2O_3 onto Ni–Al catalyst affected the hydrogen yield while, they also conducted non-catalytic steam reforming and confirmed that the H_2, CO_2 yields were low in the absence of catalyst. Galdámez et al. [2] also noticed that the total gas yield decreased with decrease in catalyst weight. Catalysts were usually reduced for an hour at high temperature with N_2/H_2 before their usage in experiments to increase activity. Galdámez et al. [2] reduced Ni–Al catalyst with a mixture of H_2 and N_2 gas for 1 h at 650 °C. Czernik et al. [40] and Kechagiopoulos et al. [16] used nickel-based naphtha reforming catalyst to produce hydrogen. Kechagiopoulos et al. [16] used C11-NK catalyst which has higher potassium content compared to other Ni catalysts. The higher potassium content plays a vital role in suppressing the coke formation and a 90% hydrogen yield was reported for the equimolar mixture of model compounds [16]. Pan et al. [9] employed C12A7-Mg catalyst and determined its lifetime to be about 210 min at 750 °C. Steam reforming of bio-oil at 750 °C using this catalyst resulted in a hydrogen yield of 80%. Wang et al. [8] conducted reforming over three catalysts: C12A7/15% Mg, 12% Ni/gamma-Al_2O_3, and 1% Pt/gamma-Al_2O_3 at 650 °C and the observed hydrogen yields were 56.7%, 58.1%, and 66.8%, respectively. Yan et al. [42] reformed bio-oil with commercial Z417 catalyst along with CO_2 sequestration using calcined dolomite and reported a hydrogen yield of about 75%. Lin et al. [14] performed catalytic reforming of bio-oil over CoZnAl catalyst electrochemically by passing ac current in a Ni–Cr wire entwined around the catalytic column. A detailed comparison of different studies in reforming of bio-oil has been made in Table 3.

The reactors usually used are fluidized bed, bench-scale, and fixed bed reactors. From the table we can observe that model compounds are usually used, though a few of them have used aqueous fraction of bio-oil. This is attributed to the complex composition of bio-oils which form residual solids on heating. A common problem experienced in the above cases is coking.

5.1. Catalysts characterization

Galdámez et al. [2] characterized Ni–Al catalyst using inductively coupled plasma (ICP), X-ray diffraction (XRD), nitrogen adsorption and temperature-programmed reduction (TPR) and found the surface area of the catalyst to be 150 m^2/g. When the catalyst was loaded with 8% and 12% La_2O_3 its surface area reduced to 141 and 131 m^2/g, respectively. Yan et al. [42] used differential thermogravimetric (DTG) and differential scanning calorimetric (DSC) curves to determine the decomposition mechanism of their sorbent dolomite. Pan et al. [9] used XPS to study their catalyst before and after steam reforming and found that there was an increase in carbon content on the surface of the catalyst after reforming. Lin et al. [14] used N_2 physisorption to determine Brunauer–Emmett–Teller (BET) and pore volume of the catalyst. Wang et al. [8] measured Mg, Ni and Pt contents in the catalyst using inductively coupled plasma (ICP) and atomic emission spectroscopy (AES). They also used XRD and N_2 physisorption at 196 °C to determine the surface atomic composition, BET surface area and pore volume. A summary of analysis techniques used is given below. BET is used to determine the surface area of the catalyst. ICP is used to determine the metal and non-metal concentrations in the catalyst while XPS is used to determine the composition of the catalysts on the surface and different states of the metal used for catalyst. The temperature effects

Table 3
Comparison study of reforming techniques discussed in the literature.

Catalyst	Experimental conditions	Key findings	Fuel type	Reference
Ni–Al promoted with La	Reactor: fluidized bed T = 450–700 °C S/C: 5.58 Liquid feeding rate: 1.84–2.94 g/min	Use of catalyst showed an increase in total gas and H_2 yield. Promotion with La did not affect H_2 yield with Ni––Al catalyst. H_2 yield: 0.029 g/g of acetic acid at 1.84 g/min feeding rate and 650 °C	Model compound: acetic acid	[2]
Commercial catalyst Z417	Reactor: bench-scale fixed bed Temperature: 500–700 °C	Optimum temperature with CO_2 capture: 550–650 °C water: bio-oil ratio-1:1 Use of dolomite to capture CO_2 showed highest H_2 yield. H_2 yield: 75% at 600 °C	Aqueous fraction of bio-oil	[42]
Ni based catalyst	Reactor: fixed bed Temperature: 600–900 °C H_2O/C: 2–8.2 G_{C1} HSV: 300–500 h^{-1}	The high potassium content in the catalyst suppressed coking. A H_2 yield of 60% was reported when aqueous phase of bio-oil was reformed, but 90% yield was reported for the model compounds at temperatures higher than 600 °C.	Model compounds: acetic acid, acetone, and ethylene and aqueous phase of bio-oil	[16]
Ru/Mgo/Al_2O_3	Reactor: Nozzle fed reactor T: 800 °C P: 1 atm S/C: 7.2	Role of MgO is vital in converting CO to CO_2 and enhancing steam adsorption capacity of the catalyst. The selectivity of H_2 in the form of pellets was the highest and was close to 100%	Model compound: acetic acid and aqueous phase of bio-‘oil	[28]
C12A7 doped with 15% Mg, 12% Ni/γ-Al_2O_3 and 1% Pt/γ-Al_2O_3	Reactor: fixed-bed flow reactor T: 750 °C S/C: 6.0 GHSV: 26,000 h^{-1}	C12A7/15% Mg exhibited high reforming activity, a H_2 yield of 71% and carbon conversion of 93%	Volatile organic components of crude bio-oil	[8]
Ni/CeO_2–ZrO_2	Reactor: fixed bed Temperate: 450–800 °C Water/bio-oil: 4.9 Ni-12% Ce-7.5%	Highest H_2 yield of 69.7% was achieved when T = 800 °C, W/B = 4.9, Ni-12% and Ce-7.5%. Under same conditions H_2 yield was higher than commercial Z417 catalyst	Aqueous fraction of bio-oil	[11]
Ni, Rh or Ir supported on calcium aluminates	Reactor: fixed bed quartz reactor Temperature: 550–750 °C S/C: 3 Space velocity: 30,000 h^{-1}	Coke deposition over Ni loaded catalyst was higher than that with the Rh or Ir. The Highest H_2 yield was obtained with 5% Ni/CaO·2Al_2O_3 catalyst and was about 70% at 750 °C for acetone	Model compounds: acetic acid and acetone	[43]
Ni–Al catalyst modified with Mg and Ca	Reactor: fluidized bed Temperature: 650 °C G_{C1}HSV: 11,800 h^{-1}	Coke formation was reduced by decreased space velocity and increased O_2. Mg modified catalyst performed better than Ca modified catalyst. A hydrogen yield of 0.1056 g/g of organics was reported for Magnesium modified catalyst.	Aqueous fraction	[44]
Commercial catalyst C11-NK and NREL#20	Reactor: bench-scale fluidized bed Temperature: 850 °C S/C: 5.8 Space velocity: 920 h^{-1}	Steam reforming resulted in a H_2 yield of about 70–80%	Whole bio-oil	[45]
C12A7 doped with 18% Mg, C12A7 doped with 25% K, C12A7, C12A7 doped with 12% Ce, C12A7 doped with 12% Mg, Al_2O_3 doped with 12% Mg, Al_2O_3 doped with 18% Mg	Temperature: 200–750 °C S/C: 1.5–9 Gas hourly space velocity(GSHV): 10,000 h^{-1} Reactor: fixed bed micro-reactor Pressure: atmospheric pressure	At 750 °C, S/C > 4, GHSV of 10,000 h^{-1} C12A718% Mg showed the highest hydrogen yield of 80% and carbon conversion of 96%	Whole bio-oil	[46]
Non-catalytic	Temperature: 625–850 °C O:C (oxygen to carbon ratio): 1.4–1.6 Reactor: tubular reactor	The partial oxidation resulted in a hydrogen yield of about 25%	Whole bio-oil	[31]

on the catalyst are determined using DTG and DSC curves. XRD is done to get an idea about the crystallographic atomic structure of the catalyst.

6. Experimental conditions

Since bio-oil is a complex mixture of many organic compounds, its steam reforming has been usually studied by either using its aqueous fraction or by using model compounds. Chornet and co-workers [6] conducted experiments with aqueous fraction of bio-oil. Many researchers have investigated H_2 production with acetic acid as a model compound [6,37,38]. Takanabe et al. [47] have studied steam reforming of acetic acid over Pt/ZrO_2. Kechagiopoulos et al. [16] used three model compounds for their investigation: acetic acid, acetone and ethylene glycol. Adhikari et al. [48] tested different noble metal based catalysts for steam reforming of glycerol.

6.1. Choice of reactor

Type of reactor plays a vital role in steam reforming of bio-oil. Fixed reactors are not preferred for steam reforming of bio-oils, since the operating time is limited due to formation of carbonaceous deposits [2]. They were prescribed to be unfit for thermally unstable biomass liquids by Czernik et al. [40] who in turn used a fluidized bed reformer. Fluidized bed on the contrary, ensured continuous operation by gasification of carbonaceous deposits on catalyst particles [2]. Basagiannis et al. [28] established that using a nozzle-fed reactor, in which the liquid is fed into the reactor using high flow rate nozzles, decreased the carbon deposition to a great

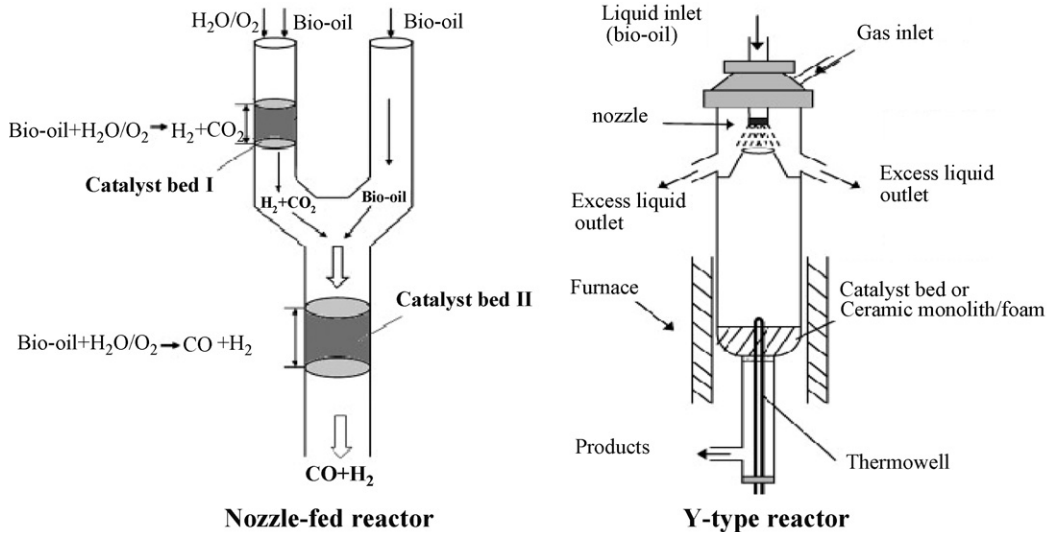


Fig. 1. Schematic representation of unique reactors used Ref. [49].

extent. Gongxuan et al. [49] performed a coupled steam reforming of bio-oil in a Y-type reactor design in which the catalyst bed was in the center and bio-oil and bio-oil mixed with steam/water were sent through the other inlets. The important factors that affect H_2 production are temperature, steam: carbon ratio, and space velocity. Fig. 1 depicts the nozzle-fed and Y-type reactors used for bio-oil reforming.

6.2. *Temperature and S/C ratio*

Since the steam reforming of bio-oils is accompanied by decrease in temperature, an increase in temperature shifts the equilibrium towards the right thereby leading to increase in H_2 yield. Similarly, the steam to carbon ration also affects H_2 yield to a great extent. Wang et al. [8] observed that H_2 production increased with increase in temperature and S/C ratio. This was accompanied with an increase in carbon conversion which was only 15% at 500 °C but later on increased to 93% at 750 °C. As S/C was increased from 1.5 to 6, both H_2 yield and carbon conversion increased. Galdámez et al. [2] conducted studies at 650 °C and 13,000 h^{-1} space velocity using a fluidized bed reactor. Yan et al. [42] carried out steam reforming of bio-oil aqueous fraction in a fixed bed reactor with CO_2 capture (using CaO and dolomite). Interestingly, they found out that H_2 production decreased at high temperatures with the capture of CO_2. The optimal temperature as reported by them for H_2 production with CO_2 capture is between 550 °C and 650 °C. Kechagiopoulos et al. [16] observed an increase in H_2 yield with increase in H_2O/C ratios and decrease in pressure. They also found that the maximum yield for their experimental conditions was between 600 and 750 °C. Czernik et al. [40] carried out steam reforming at temperatures 800–850 °C, S/C range of 7–9 and space velocity of 700–1000 h^{-1}. Pan et al. [9] conducted steam reforming of bio-oils in a fixed bed micro-reactor where in the vaporized bio-oil was fed into the reactor at a space velocity of 10,000 h^{-1}. They performed experiments in the temperature range 550–750 °C at S/C 4.0.

The effect of liquid feed rate has been well addressed by Galdámez et al. [2] with respect to their experimental conditions. The residence time decreases as the liquid feed rate increases which should eventually result in lower H_2 yield. But, the result obtained indicated higher H_2 yield. This was due to the increase in partial pressure in the reaction bed with higher liquid feed rate. The typical residence time used was in the range 0.56–0.44 s. Since the rate of the reaction was directly dependent on reactant concentration, higher partial pressure resulted in higher H_2 yield.

Kechagiopoulos et al. [16] reported a low hydrogen yield of about 60% by reforming the aqueous phase of bio-oil. Wang et al. [8] performed reforming over three different catalysts (C12A7/15% Mg, 12% Ni/γ-Al_2O_3, and 1% Pt/γ-Al_2O_3), and found that at 700 °C 1% Pt/γ-Al_2O_3 showed the highest H_2 yield of 75%. Pan et al. [9] reported a maximum carbon conversion and H_2 yield of about 95% and 80% at 750 °C, respectively which were higher than that obtained with naphtha and CH_4.

6.3. *Other methods of hydrogen production*

Apart from steam reforming, there are other techniques being used for hydrogen production from bio-oil. Although not all the available processes have been tested, the paper briefly discussed below to demonstrate techniques that are relevant to produce hydrogen using bio-oil.

6.3.1. *Partial oxidation*

In this method, the substrate is oxidized with oxygen (in the presence or in the absence of catalyst), resulting in high temperature which in turn balances the energy required for the process. However, excess air leads to complete oxidation of the substrate resulting in formation of CO_2 and water [27].

$$\text{(Substrate)}\,C_nH_mO_k + \text{air} \rightarrow \text{carbonoxides} + H_2 + N_2 \tag{4}$$

Marda et al. [31] conducted non-catalytic partial oxidation of bio-oil, while Rennard et al. [32] performed autothermal catalytic partial oxidation of bio-oil using esters and acids as model compounds over platinum and rhodium based catalysts. Marda et al. [31] reported a low H_2 yield of about 25% while Rennard et al. [32] have concentrated on synthesis gas production.

6.3.2. *Autothermal reforming*

It is a combination of steam reforming and partial oxidation techniques in which the substrate is reformed in the presence of air and water to produce H_2.

$$\text{(Substrate)}\,C_nH_mO_k + \text{air} + \text{steam} \rightarrow CO + H_2 + N_2 \tag{5}$$

The advantage lies in the fact that the process does not require energy ideally because all heat produced during the oxidation step

is consumed by steam reforming step. However, low H_2 yield compared to steam reforming process is a disadvantage of autothermal reforming.

Vagia et al. [35] performed thermodynamic analysis of autothermal reforming of selected components of aqueous bio-oil fraction to determine the optimum amount of oxygen required to carry out an energy neutral process. They also studied the effect of temperature and pressure on H_2 production. They reported that at optimum operating conditions, 1 kmol of H_2 is produced from 0.245 kmol of bio-oil, which is 20% lower than the H_2 yield obtained by steam reforming method.

6.3.3. Aqueous-phase reforming

This process which was developed by Dumesic and his coworkers is carried out at high pressure (at around 60 bar) and low temperature (at around 270 °C) [50]. The advantages of this process are it produces low amount of CO and the process takes place in liquid phase (while the others take place in gas phase) so there is no need to vaporize the substrate used for producing hydrogen. The effect of catalyst size with pure and crude glycerol was studied by Claus and Lehnert [51] and the study revealed that H_2 selectivity was higher for larger particles. Iriondo et al. [52] used different promoters and found that Ni catalyst does not work very well for glycerol due to severe deactivation.

6.3.4. Supercritical water reforming

Water when heated and compressed to its critical temperature (374 °C) and pressure 22.1 MPa becomes supercritical water. Supercritical water possesses characteristics of both liquid water and vapor which includes densities, viscosities, high diffusivity and good transporting properties [53,54]. Penninger and Rep [55] conducted supercritical water reforming of aqueous wood pyrolysis condensate obtained from moist beech wood saw dust at 650 °C and 28 MPa. They found that, there was no plugging at 28 MPa pressure and a small percentage of soda (0.1%) promoted hydrogen production. A hydrogen yield of 36.6 vol% was observed at a residence time of 12.5 s and a total feed flow of 690 g/h. Byrd et al. [56] studied hydrogen production from switchgrass biocrude by catalytic gasification in supercritical water. The Ni, Co, Ru catalysts supported on TiO_2, ZrO_2 and $MgAl_2O_4$ were tested and among them Ni/ZrO_2 exhibited highest hydrogen yield of 0.98 mol H_2/mol C at 600 °C and 250 bar. Yu et al. [57] and Antal et al. [58] reformed wet biomass to hydrogen, carbon dioxide and carbon monoxide using supercritical water at 600 °C and 35 MPa. Gupta and co workers carried out supercritical water reforming of glycerol over Ru/Al_2O_3 catalyst which yielded 6.5 mol of H_2/mol of glycerol [33].

6.3.5. Sequential cracking

It is a two step process in which the bio-oil is first catalytically cracked/reformed without addition of water followed by subsequent regeneration of the catalyst with oxygen [59]. Reactions to demonstrate the technique are given below taking methane as an example [60–65]:

$$\text{Cracking}: CH_4 \rightarrow C + 2H_2 \quad (6)$$

$$\text{Regeneration}: C + O_2 \rightarrow CO_2 \quad (7)$$

Davidian et al. [59] used two Ni based catalyst and found them to be performing very well for producing hydrogen from bio-oil. Iojoiu et al. [66] used Pt and Rh catalysts supported in ceria–zirconia for H_2 production from bio-oil obtained from beech wood residues. From the heat balance calculations, they also established that sequential cracking process could be operated auto-thermally. The possibility of removing large carbon deposits by catalyst regeneration is a great advantage of this method despite the reported sintering of ceria–zirconia support. The H_2 productivity was only 18 mmol $H_2\,g^{-1}$ as compared to 20 and 37 mmol $H_2\,g^{-1}$ (at 2.5 and 10 H_2O/C ratios) productivities in steam reforming method. The operating temperature was 700 °C and H_2 yield observed was 40%.

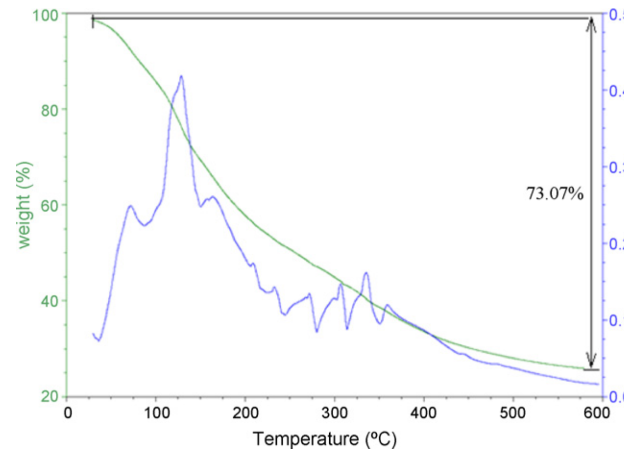


Fig. 2. TGA results for bio-oil produced from pine wood.

7. Challenges and conclusions

Coking is a major problem that is encountered in steam reforming process. It results from thermal decomposition of organic compounds onto the catalyst resulting in its deactivation [16].

$$C_nH_mO_k \rightarrow C_xH_yO_z + \text{Gas}\,(H_2,\ CO,\ CO_2,\ CH_4\ldots) + \text{Coke} \quad (8)$$

Thermogravimetric analysis (TGA) revealed that there is a maximum weight loss at 125 °C, which could be mainly due to vaporization of water. At temperatures higher than 400 °C, the weight loss decreased gradually and when the temperature reached 600 °C there was no weight loss observed. From the TGA graph (Fig. 2), it can be seen that there is a total weight loss of 73.07% at 600 °C, which means that 26.93% of the bio-oil fed into the reactor did not vaporize, and hence would result in clogging of catalyst's pores and the reactor. Bio-oil cannot be completely vaporized, and when heated, leads to the formation of residual solids. To overcome this operational difficulty while feeding, Basagiannis et al. [28] used a nozzle injection system to spray bio-oil into the reactor. This problem can also be avoided by increasing the temperature so that gasification of the carbonaceous deposits takes place thereby resulting in regeneration of the catalyst. Rennard et al. [30] established that high steam to carbon ratio helps decreasing coke formation. However, the heat load increases, since more steam has to be supplied. Coke formation is also reduced by blending of bio-oil [30]. Oxidation of coke also helps in alleviating coking, although the presence of oxygen results in decreased experimental and theoretical H_2 yields [66–70]. Medrano et al. [44] reported that the coke formation decreased from 149 mg C/g catalyst to 73 mg C/g catalyst with an addition of 4% oxygen. The use of $Ce_{1-x}Ni_xO_{2-y}$ as catalyst is also known to decrease the formation of carbonaceous deposits due to Ce, O, Ni interaction [71]. A catalyst ($Ce_{0.8}Ni_{0.2}O_{2-y}$) prepared using adapted micro emulsion method proved to be an excellent catalyst for ethanol steam reforming. It was not only less expensive than Rh/CeO_2 catalyst, but also has a higher catalytic activity [72].

Estimating the world's current energy demands and foreseeing the demands in the upcoming years we realize the need for a pollution-free alternative source of energy. Hydrogen obtained from bio-oil would serve as a versatile energy carrier in this regard. The purpose of this review is to give a comprehensive update of various developments in the field of hydrogen production from bio-oil. Though we have specifically documented an overview of

steam reforming of bio-oil, we have also discussed other methods like partial oxidation, autothermal, aqueous phase reforming and supercritical water reforming to show their differences. Quite a lot of work has been reported in the literature on steam reforming of bio-oil though, to the best of our knowledge, very few have been reported on aqueous phase reforming of bio-oils. Experiments have been conducted to check the change in H_2 yield with different catalysts, reactors at wide range of temperatures. Further emphasis must be given to the catalyst deactivation issue and ways to overcome the coking challenge during bio-oils reforming must be explored.

References

[1] Haryanto A, Fernando S, Murali N, Adhikari S. Energy Fuels 2005;19:2098–106.
[2] Galdámez J, García L, Bilbao R. Energy Fuels 2005;19:1133–42.
[3] Babu B, Biofuels. Bioprod Biorefin 2008;2:393–414.
[4] Bridgwater A, Meier D, Radlein D. Org Geochem 1999;30:1479–93.
[5] Lu Q, Li W, Zhu X. Energy Convers Manage 2009;50:1376–83.
[6] Wang D, Czernik S, Montane D, Mann M, Chornet E. Ind Eng Chem Res 1997;36:1507–18.
[7] Sipilä K, Kuoppala E, Fagernäs L, Oasmaa A. Biomass Bioenergy 1998;14:103–13.
[8] Wang Z, Dong T, Yuan L, Kan T, Zhu X, Torimoto Y, et al. Energy Fuels 2007;21:2421–32.
[9] Pan Y, Wang Z, Kan T, Zhu X, Li Q. Chin J Chem Phys 2006;19:190.
[10] Mullen C, Boateng A, Goldberg N, Lima I, Laird D, Hicks K. Biomass Bioenergy 2010;34:67–74.
[11] Yan C, Cheng F, Hu R, Fu P. Int J Hydrogen Energy 2010;35:2612–6.
[12] Tsai WT, Lee MK, Chang YM. Bioresour Technol 2007;98:22–8.
[13] Torri C, Reinikainen M, Lindfors C, Fabbri D, Oasmaa A, Kuoppala E. J Anal Appl Pyrolysis 2010;88:7–13.
[14] Lin S, Ye T, Yuan L, Hou T, Li Q. Chin J Chem Phys 2010;23:451.
[15] Agblevor FA, Mante O, Abdoulmoumine N, McClung R. Energy Fuels 2010;24:4087–9.
[16] Kechagiopoulos P, Voutetakis S, Lemonidou A, Vasalos I. Energy Fuels 2006;20:2155–63.
[17] Mullen C, Boateng A, Hicks K, Goldberg N, Moreau R. Energy Fuels 2009;24:699–706.
[18] Mante OD, Agblevor FA. Waste Manage 2010;30:2537–47.
[19] Mohan D, Pittman Jr CU, Steele PH. Energy Fuels 2006;20:848–89.
[20] Mohan D, Pittman CU, Steele PH. Energy Fuels 2006;20:848–89.
[21] Armaroli N, Balzani V. ChemSusChem 2011;4:21–36.
[22] Rand D, Dell R, Dell R. Hydrogen energy: challenges and prospects. Royal Society of Chemistry; 2008.
[23] In: Borgschulte A, Zuttel A, Schlapbach L, editors. Hydrogen as a future energy carrier Weinheim; 2008.
[24] Svoboda K, Pohorelý M, Hartman M, Martinec J. Fuel Process Technol 2009;90:629–35.
[25] Navarro R, Pena M, Fierro J. Chem Rev 2007;107:3952–91.
[26] Rostrup-Nielson J. In: Anderson JR, Boudart M, editors. Catalysis, Science and Technology, vol. 5. Berlin: Springer; 1984. pp. 1–117.
[27] Adhikari S, Fernando S, Haryanto A. Energy Convers Manage 2009;50:2600–4.
[28] Basagiannis A, Verykios X. Catal Today 2007;127:256–64.
[29] Shuler M, Kargi F. Bioprocess engineering. NJ: Prentice Hall Upper Saddle River; 2002.
[30] Rennard D, French R, Czernik S, Josephson T, Schmidt L. Int J Hydrogen Energy 2010;35:4048–59.
[31] Marda J, DiBenedetto J, McKibben S, Evans R, Czernik S, French R, et al. Int J Hydrogen Energy 2009;34:8519–34.
[32] Rennard D, Dauenhauer P, Tupy S, Schmidt L. Energy Fuels 2008;22:1318–27.
[33] Byrd A, Pant K, Gupta R. Fuel 2008;87:2956–60.
[34] Vagia E, Lemonidou A. Int J Hydrogen Energy 2007;32:212–23.
[35] Vagia E, Lemonidou A. Int J Hydrogen Energy 2008;33:2489–500.
[36] Aktas S, Karakaya M, AvcI. A. Int J Hydrogen Energy 2009;34:1752–9.
[37] Wang D, Montane D, Chornet E. Appl Catal A: Gen 1996;143:245–70.
[38] Marquevich M, Czernik S, Chornet E, Montané D. Energy Fuels 1999;13:1160–6.
[39] Garcia L, French R, Czernik S, Chornet E. Appl Catal A: Gen 2000;201:225–39.
[40] Czernik S, French R, Feik C, Chornet E. Ind Eng Chem Res 2002;41:4209–15.
[41] Wang D, Czernik S, Chornet E. Energy Fuels 1998;12:19–24.
[42] Yan C, Hu E, Cai C. Int J Hydrogen Energy 2010;35:2612–6.
[43] Vagia E, Lemonidou A. Appl Catal A: Gen 2008;351:111–21.
[44] Medrano J, Oliva M, Ruiz J, García L, Arauzo J. Energy; 2010.
[45] Czernik S, Evans R, French R. Catal Today 2007;129:265–8.
[46] Wang Z, Pan Y, Dong T, Zhu X, Kan T, Yuan L, et al. Appl Catal A: Gen 2007;320:24–34.
[47] Takanabe K, Aika K, Seshan K, Lefferts L. J Catal 2004;227:101–8.
[48] Adhikari S, Fernando S, Haryanto A. Catal Today 2007;129:355–64.
[49] Gongxuan H. Int J Hydrogen Energy 2010;35:7169–76.
[50] Cortright R, Davda R, Dumesic J. Nature 2002;418:964–7.
[51] Lehnert K, Claus P. Catal Commun 2008;9:2543–6.
[52] Iriondo A, Barrio V, Cambra J, Arias P, Güemez M, Navarro R, et al. Top Catal 2008;49:46–58.
[53] Loppinet Serani A, Aymonier C, Cansell F. ChemSusChem 2008;1:486–503.
[54] Kobe Steel L, Characteristics and uses of supercritical water 2011.
[55] Penninger JML, Rep M. Int J Hydrogen Energy 2006;31:1597–606.
[56] Byrd AJ, Kumar S, Kong L, Ramsurn H, Gupta RB. Int J Hydrogen Energy 2011;36:3426–33.
[57] Yu D, Aihara M, Antal MJ. Energy Fuels 1993;7:574–7.
[58] Antal Jr M, Manarungson S, Mok W, Bridgwater A. Advances in thermochemical biomass conversion, vol. 2; 1994. p. 1367–77.
[59] Davidian T, Guilhaume N, Iojoiu E, Provendier H, Mirodatos C. Appl Catal B: Environ 2007;73:116–27.
[60] Choudhary TV, Goodman DW. J Catal 2000;192:316–21.
[61] Choudhary T, Sivadinarayana C, Chusuei C, Klinghoffer A, Goodman D. J Catal 2001;199:9–18.
[62] Aiello R, Fiscus J, Zur Loye H, Amiridis M. Appl Catal A: Gen 2000;192:227–34.
[63] Takenaka S, Kato E, Tomikubo Y, Otsuka K. J Catal 2003;219:176–85.
[64] Villacampa JI, Royo C, Romeo E, Montoya JA, Del Angel P, Monzón A. Appl Catal A: Gen 2003;252:363–83.
[65] Odier E, Schuurman Y, Barrai K, Mirodatos C. In: Xinhe B, Yide X, editors. Studies in surface science and catalysis. 2004. p. 79–84.
[66] Iojoiu E, Domine M, Davidian T, Guilhaume N, Mirodatos C. Appl Catal A: Gen 2007;323:147–61.
[67] Domine M, Iojoiu E, Davidian T, Guilhaume N, Mirodatos C. Catal Today 2008;133:565–73.
[68] Kechagiopoulos P, Voutetakis S, Lemonidou A, Vasalos I. Ind Eng Chem Res 2008;48:1400–8.
[69] van Rossum G, Kersten S, van Swaaij W. Ind Eng Chem Res 2007;46: 3959–67.
[70] Rioche C, Kulkarni S, Meunier F, Breen J, Burch R. Appl Catal B: Environ 2005;61:130–9.
[71] Barrio L, Kubacka A, Zhou G, Estrella M, Martiĭnez-Arias A, Hanson JC, et al. J Phys Chem C 2010;114:12689–97.
[72] Zhou G, Barrio L, Agnoli S, Senanayake S, Evans J, Kubacka A, et al. Angewandte Chemie 2010;122:9874–8.